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DE-A- 2 156 858
US-A- 3 478 003
US-A- 3 503 946

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Description

INTRODUCTION

The synthesis of water-soluble polymers has generally been limited to the use of certain vinyl monomers containing the various functional groups such as carboxylate, amide and sulfate. Examples of these monomers are acrylic acid, acrylamide, and AMPS (2-acrylamido-2-methyl propane sulfonic acid). In addition, the synthesis of vinylic water-soluble polymers containing other functional groups has been limited from the point of view that only certain of these kinds of monomers are commercially produced.

As a result, the use of these water-soluble polymers is limited to the structures mentioned above or similarly modified structures thereof. It would, therefore, be an advance in the art if other water-soluble, vinylic, polymeric chemical structures could be synthesized on a vinylic polymeric backbone which structures would contain other functional groups, such as alcohol or ether groups, or for example ethoxylate groups, and which structures might also contain other functional groups which could enhance the use of these water-soluble polymers in certain applications such as dispersants in water treatment, scale inhibitors in natural and industrial waters, flocculants, coagulants and thickeners.

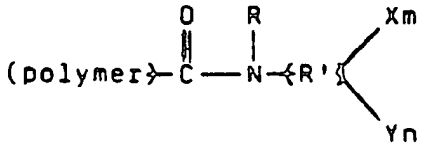
From US-A-34 78 003 it has been known to prepare water-soluble cationic polyacrylamides useful as flocculants by chemical modification of a polyacrylamide by transamidation with a diamine. The transamidation is carried out in a glycol and a portion of the glycol is incorporated in the cationic product as an ester. From US-A-25 03 946 it has been known to provide a process for the manufacture of cationic polyacrylamide, wherein polyacrylamide is heated with a water-soluble polyamine having not more than one amide-reactive substituent at least until the polyacrylamide has become cationic. The resulting cationic polyacrylamide may be purified of any unreacted amine and solvent present, and is useful as flocculating agent for suspended matter in aqueous suspension.

It is, therefore, an object of this invention to create water-soluble polymers containing alkoxylate, tertiary or quaternary amine functional groups and mixtures thereof ; and in addition, which polymers may also contain other functional groups which may be useful when applied to aqueous solutions or environments ; as well as a process which can generally be applicable to the synthesis of various types of water-soluble polymers containing the alcohol or alkoxylate functional groups with or without the additional presence of other functional groups which may be useful when these polymers are added to aqueous systems.

THE INVENTION

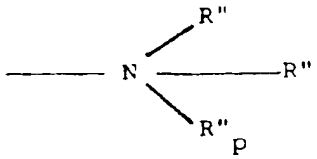
The invention is concerned with a process for modifying water-soluble polymers containing pendant amide functional groups, such polymers being primarily derived from acrylamide containing vinylic polymers/copolymers or from alkyl substituted acrylamide containing vinylic polymers or copolymers, and which polymers/copolymers are water soluble and contain pendant amide functional groups derived from acrylamide, methyl acrylamide and ethylacrylamide.

The water soluble pendant amide and/or substituted amide containing polymers and/or copolymers of the invention have a molecular weight of at least 500 and also have at least 1 mole percent (1%) of any original pendant amide group converted to pendant substituted amide groups represented by the structure :

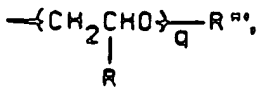


wherein : R is individually chosen, at each occurrence, from hydrogen or a lower alkyl (C_1-C_4) group ; R' is a multivalent (capable of multiple covalent bonding to various and numerous functional groups) hydrocarbon bridging group having from 1-20 carbon atoms, which bridging groups may be chosen from linear alkyl, branched alkyl, aryl, alkaryl, cyclic, and heterocyclic groups, and/or mixtures thereof ;

X is represented by :

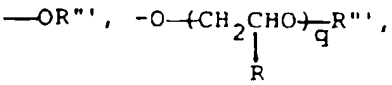


wherein R" is a hydrocarbon functional group individually chosen, at each occurrence, from linear alkyl, branched alkyl, aryl, alkaryl, cyclic, heterocyclic groups, or two R" groups taken together to form a ring, and alkoxyl groups represented by :



and mixtures thereof ;

Y is individually chosen, at each occurrence, from



and mixtures thereof ;

R"' is individually chosen, at each occurrence, from hydrogen or hydrocarbon groups having from 1 to 20 carbon atoms and being linear alkyl, branched alkyl, aryl and alkaryl groups, cyclic and heterocyclic groups and mixtures thereof ;

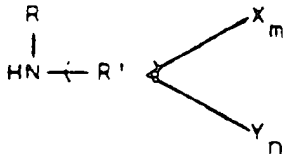
m = 0 – 20 ;

n = 1 – 20 ;

p is 0 or 1, provided that when p is 1, an electroneutralizing gegenion is equivalently present ; and

q = 1 – 50.

In the inventive process the equivalent of a transamidation reaction is used with any pendant amide group on a polymer using a chemical reactant represented by the structure :



(I)

wherein R, R', X, Y, m and n have the meanings described above.

The chemical reactant described above is primarily a reactive amino substituted compound which also contains the alkoxylate functional group, and/or the tertiary and quaternary amine functional groups, and mixtures thereof ; and wherein the reactive amine functional group contains at least 1 active hydrogen substituted on the amino nitrogen. Although substituted amine compounds having both primary and secondary amines can react with pendant amide functionality on polymers via the transamidation reaction conditions to achieve modified pendant amide types of polymers, it is preferable that when a secondary amine is chosen to accomplish this modification of pendant amide containing polymers, that the alkyl group substituted on the reactive amino nitrogen contain no more than 4 carbon atoms, i.e. the alkyl substitution should be limited to methyl, ethyl, propyl and butyl functionality, and isomers thereof. Tertiary amines and quaternary ammonium functionality are not reactive in the transamidation reaction.

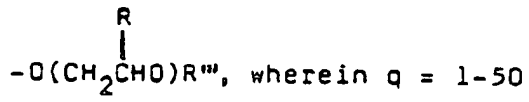
However, it is most preferred that the reactive amine substitution on the chemical reactant be a primary amino functional group. When a primary amino functional group is used to accomplish the transamidation reaction, the reaction easily proceeds so as to incorporate at least 2, and preferably from 25-60, mole percent of the chemical reactant used into the water-soluble polymer chain containing pendant amide groups, substituting therefore a substituted amide group containing an alkoxylate group, a tertiary amino group, a quaternary

ammonium group, or mixtures thereof, for what was originally the pendant amide functionality.

In addition to the reactive amine substitution in the chemical reactant described above, this chemical reactant containing at least 1 alkoxylate group may also contain at least 1 tertiary amino group, at least 1 quaternary ammonium group, or may contain admixtures of any or all of these functional groups.

In addition to the alkoxylate functional group and the reactive amine functional group, the chemical reactant may also contain other functional groups chosen from the group consisting of ether groups, tertiary amino and quaternary ammonium groups and mixtures thereof. Preferably, the chemical reactant is limited to contain a reactive primary amino group responsible for the transamidation reaction, at least 1 alkoxylate group which allows the formation of an alkoxylated water-soluble polymer, and/or a tertiary amino group, or a quaternary ammonium functional group, the presence of which, separately or in combination, may enhance the activity of water-soluble alkoxylate containing polymers synthesized by the process.

Most preferably, the chemical reactant contains a primary amine, 1 or more tertiary amino groups, and 1 or more alkoxylate groups which may contain from 1 to 50 repeating units of the structure :

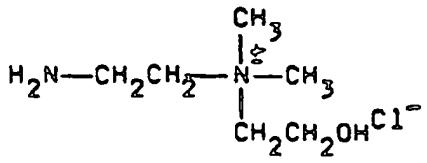


$$-O(CH_2\underset{\displaystyle R}{\underset{|}{C}}HO)R''', \text{ wherein } q = 1\text{-}50$$

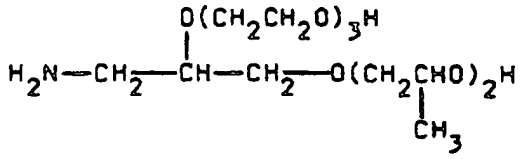
and R and R''' have the meanings above.

Several preferred species of the chemical reactant described above are demonstrated in the following formulations :

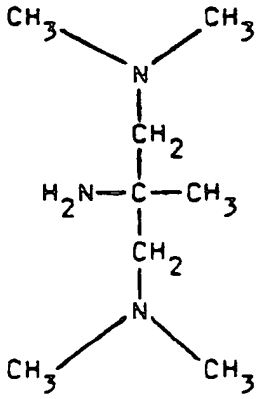
a)



b)

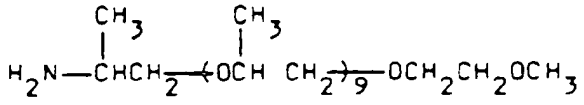


c)

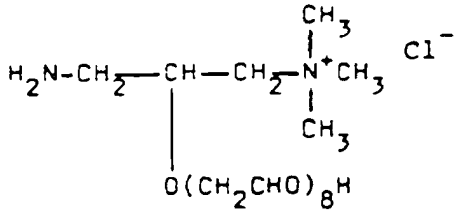


(II)

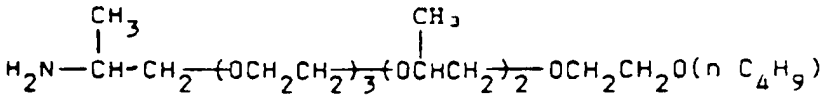
d)



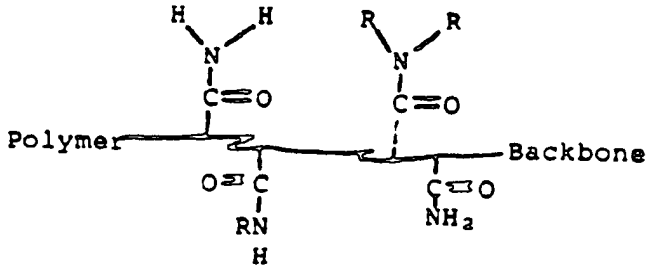
e)



f)



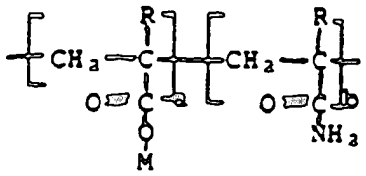
The pendant acrylamide containing polymers are water-soluble polymers which have a general structure allowing the presence of a pendant amide group as demonstrated in Formula III :



(III)

In Formula III, as one can observe, the pendant amide group may be a primary amide, a secondary amide, or a tertiary amide compound and mixtures thereof. Preferably, to obtain reasonable conversions of these pendant amide groups to the alkoxylate, tertiary amino, or quaternary ammonium or mixtures thereof, functional groups described above, the pendant amide group is a primary amide group.

The most likely water-soluble polymers containing pendant amide functionality which polymers are easily modified under the conditions of the transamidation reaction, are those water-soluble polymers described by Formula IV :



(IV)

In Formula IV,

R is hydrogen or a lower alkyl group containing from 1-4 carbon atoms ;

M is hydrogen, a lower (C_1-C_4) alkyl group, an alkali metal, alkaline earth metal or ammonium ion or mixtures thereof ;

and a and b are integers having the following relationships :

a/b ranges between 0 to 100, and

a + b is sufficient so as to provide a polymer having a molecular weight of at least 500. Preferably the sum, a + b, is sufficient to provide a molecular weight ranging between 1,000 and 20 millions.

As can be seen, the polymers described above may be homopolymers of acrylamide or its alkyl homologs, such as methacrylamide, they may be copolymers of acrylamide with acrylic acid or its homologs such as methacrylic acid, or they may be terpolymers with other monomers of a vinylic nature which contain acrylamide and acrylic acid, and their homologs such as methacrylic acid, and methacrylamide.

The chemical reaction which is preferred to obtain the alkoxylated and/or cationic polymers of this invention is a reaction which can generally be referred to as a transamidation reaction. This reaction substitutes a reactive amine compound which also contains other functional groups, such as the alkoxylate function groups, for the nitrogen portion of a pendant amide group contained on a polymeric backbone as described above. This transamidation reaction has been discovered to be a general reaction which can achieve, for example, the substitution of the reactive amino containing alkoxylated reactants for the amide nitrogen group of the pendant amide functionality of a water-soluble polymer, thereby obtaining unique alkoxylated/amide containing polymers.

The reaction conditions require that polymers containing pendant amide groups be dissolved or readily dispersed in a solvent which is a common solvent for the chemical reactant of the class described above. In other words, both the polymer which is to be modified and the chemical reactant should be soluble or dispersible in the same solvent system.

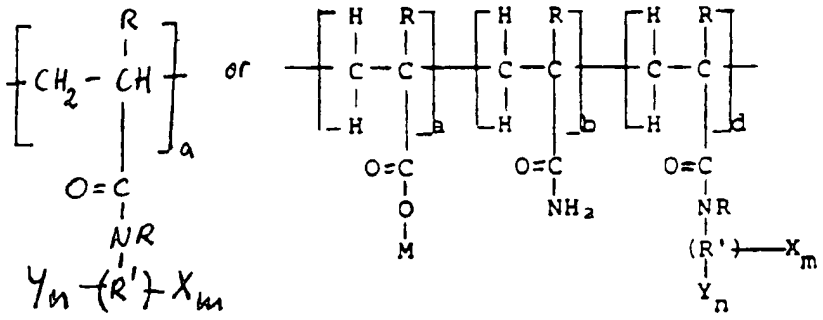
Common solvents which have been found useful in this reaction include i.a. water, dimethylformamide, dimethylsulfoxide, diglyme and admixtures thereof, and admixtures of these solvents, either singly or taken together with other miscible solvents such as ethanol, tertiary butanol and 2-methoxyethyl ether.

A preferred solvent which is a common solvent for both the polymer containing pendant amide groups and the reactive amino group chemical reactants is water, particularly if the polymer containing pendant amide group is initially water-soluble, as in the case of most acrylamide containing vinylic polymers. Another preferred common solvent for the reaction is a water-in-oil emulsion wherein the dispersed water phase contains dissolved or dispersed therein both the polymers containing pendant amide groups and the chemical reactants described above.

After having dissolved the polymers containing pendant amide groups in the common solvent, preferably water, the chemical reactant can be added to obtain a solution or dispersion of amide containing polymer and the chemical reactants of this invention. Whether the polymer or the reactant is first added to the common solvent is of no consequence. This admixture is then added to or contained in a reaction vessel capable of withstanding a pressurized chemical reaction, for example, a Parr Bomb type of vessel. The vessel is enclosed and then heated to a temperature of at least 100°C, preferably at least 110°C, and most preferably to a temperature of at least 120°C. If the temperature is increased above 100°C, the vessel contents can expand and the pressure within the vessel can exceed one atmosphere and depending upon the solvent, the chemical reactants used, can reach up to 5 to 15 bar, and possibly more. The pressure within the reaction vessel is a non-controlled variable and is controlled only to the extent that the vessel is enclosed, that a reaction temperature of at least 100°C or higher is reached, and the vessel may contain solvents or reactants of more or less volatile nature, which solvents and reactants have vapor pressures of such a nature that pressure vessels are required at temperatures above 100°C.

Once the reaction vessel contents have reached at least 100°C, and preferably 110°C, the reaction is allowed to occur for at least 3 minutes at this temperature, and preferably for whatever length of time is necessary to accomplish a minimum of at least a 25 percent conversion of the added amount of chemical reactant. The chemical reactant is, of course, converted to a pendant substituted amide which is the product of the transamidation chemical reaction summarized above. If the polymer is a homopolymer of acrylamide, methacrylamide, or a copolymer of vinyl, amide containing, monomers such that no other pendant functional group is present besides amide functional groups, the condition of the reaction is such that at least some degree of amide hydrolysis may also occur in those reactions in which water or a water containing solvent is utilized. In such cases, the final polymer product may contain a carboxylate functional group in addition to the modified substituted amide groups and any unreacted starting amide groups left from the starting polymer.

Therefore, the chemical reaction or process produces polymers having th structure :



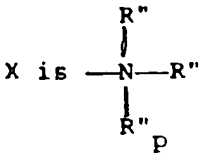
(V)

wherein

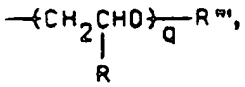
R is individually chosen, at each occurrence, from H and lower alkyl (C_1-C_4) groups ;

M is individually chosen, at each occurrence, from hydrogen, lower alkyl (C_1-C_4) groups, alkali metal, alkaline earth metal, primary, secondary and tertiary amines, and ammonium ion and mixtures thereof ;

R′ is a multi-covalent hydrocarbon bridging group having from 1 to 20 carbon atoms and being chosen from linear or branched alkyl, aryl, alkaryl cyclic and heterocyclic functional groups, and mixtures thereof ;



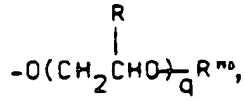
wherein R″ is a hydrocarbon functional group individually chosen, at each occurrence, from linear alkyl, branched alkyl, aryl, alkaryl, cyclic, heterocyclic groups, or 2 R″ groups taken together to form a ring, and alkoxyl groups represented by :



and mixtures thereof ;

and wherein p is 0 or 1, provided that when p is 1, an electroneutralizing gegenion is present in an equivalent amount, and wherein

Y is chosen from the group consisting of OR‴,



and mixtures thereof wherein R is as defined above ;

R‴ is individually chosen from hydrogen, or hydrocarbon groups having 1-20 carbon atoms and being chosen from linear or branched alkyl, aryl, akaryl, cyclic and heterocyclic groups, and mixtures thereof ;

a, b, and d are integers with the following relationships ;

a is at least 10

a/b = up to 100,

b/d = 0.01 to 100,

a/d = up to 100,

and the sum of a + b + d is sufficient to provide a molecular weight of at least 500, preferably 1,000 to

20,000,000.

and the ratio of d : (a + b) is from 100 : 1 to 1 : 100 ; preferably 20 : 1 to 1 : 100 ;
and wherein

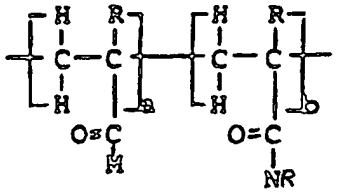
q = 1 to 50,

m = 0 to 20, preferably 0 to 10, and

n = 1 to 20, preferably 1 to 10, with the proviso that,

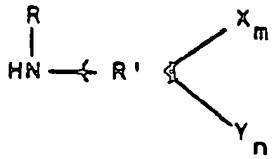
the sum of (m + n) is 1-12, when m is 0 to 10 and n is 1 to 10 ; and wherein each mer unit defined by a, b or d is randomly distributed within the polymer, which process comprises reacting, in a common solvent, at a temperature of at least 100°C in an enclosed pressurized vessel :

A. a polymer having a molecular weight of at least 500, and having pendant amide functional groups, which polymer is represented by the structure :



wherein R, M, a, b have the same meanings as above ; with,

B. a chemical reactant having the structure :

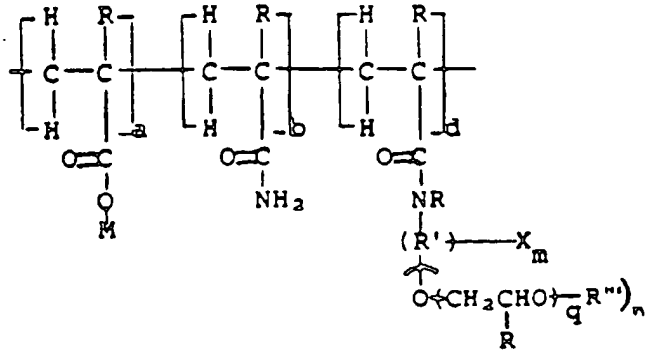


wherein R, R', X, Y, m and n, have the meanings above ; and wherein the mole ratio of chemical reactant to pendant amide groups ranges between 5 : 1 and 1 : 100 ; and the reaction occurs for an effective amount of time to accomplish at least a 25 percent conversion of chemical reactant to water-soluble substituted amide containing polymer ; and then recovering the water-soluble substituted amide containing polymer.

Polymer recovery may be accomplished in several ways known to the person familiar with the art. For example, the polymers may be precipitated by addition of precipitating solvents, or non-solvents, to the reaction mixture. For example, methanol or acetone may be added to the reaction mixture either as is or after concentration by distillation or vacuum distillation to precipitate the polymers. The polymers may also be recovered by vacuum distillation of solvent and unreacted chemical reactant from the reaction product mixture. The polymers may also be recovered by gel permeation chromatographic techniques. However, the polymers are principally recovered simply as a solution in the common solvent used to perform the transamidation reaction, and used as such.

Depending on polymer characteristics, such as degree of substitution, type of substitution and molecular weight, the polymers may be used as flocculants, coagulants, dispersants, slurry stabilizers, collectors, retention aids, dewatering aids, thickeners and scale inhibitors.

Preferably in the process according to the invention water-soluble alkoxylated polymers are produced having randomly repeated mer units represented by the formula :

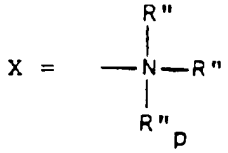


wherein

R is H or a lower alkyl (C_1-C_4) group ;

M is hydrogen, a lower alkyl (C_1-C_4) group, an alkali metal or alkaline earth metal, a tertiary amine, quaternary ammonium and ammonium ion or mixtures thereof ;

R′ is a multi-covalent hydrocarbon bridging group having from 1 to 16 carbon atoms and being chosen from linear alkyl, branched alkyl, cyclic, aromatic heterocyclic, and mixtures thereof, functional groups ;



or mixtures thereof ;

wherein

R″ and p have the meanings above, and

R‴ has the meanings described above ;

and wherein :

a, b, and d are integers with the following relationships ;

a/b = 0 to 100,

b/d = 0.01 to 100,

a/d = 0 to 100,

and the sum of a + b + d is sufficient to provide a molecular weight of at least 1,000,

and the ratio of d : (a + b) is from 100 : 1 to 1 : 100 ;

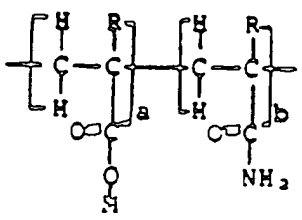
and wherein

n ranges between 1 and 20 and m ranges between 0 and 20 and

q ranges between 1 and 50 ;

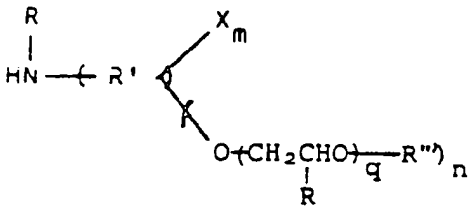
which process comprises reacting, in a common solvent, at a temperature of at least 100°C :

A. a polymer having a molecular weight of at least 500, and having pendant amide functional groups, and represented by the structure :



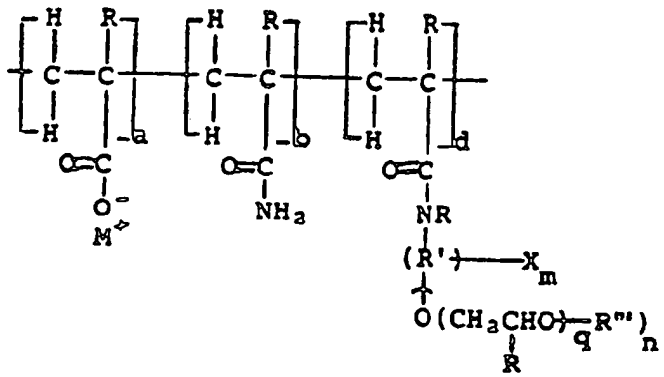
wherein R, M, a, b have the same meanings as above ; with

B. a chemical reactant having the structure :



wherein R, R', R''', X, m, n and q have the meanings above ; and wherein the mole ratio of chemical reactant to pendant amide groups ranges between 5 : 1 and 1 : 100 ; and wherein the reaction occurs for an effective amount of time to accomplish at least a 25 mole percent conversion of chemical reactant to water-soluble alkoxylated polymer ; and then recovering the water-soluble alkoxylated polymer.

Most preferably, the process is a method for the synthesis of water-soluble alkoxylated polymers represented by the formula :

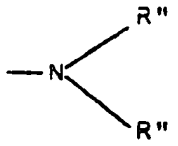
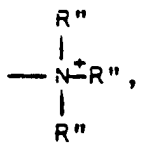


wherein

R is hydrogen or a C_1 to C_4 lower alkyl group ;

M is hydrogen, an alkali metal or ammonium ion, or mixtures thereof ;

R' is a multi-covalent, branched alkyl, linear alkyl or cyclic hydrocarbon bridging group having from 1 to 8 carbon atoms ;

X is  or  ,

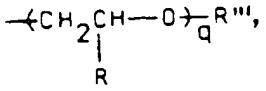
and mixtures thereof ;

n = 1 to 6 ;

m = 0 to 6 ;

q = 1 to 25 ; and

wherein R'' is a lower (C_1-C_4) group, or alkyloxylate group represented by :



and R‴ is hydrogen, or a linear or branched alkyl group, aryl group, alkaryl group, cyclic group or mixtures thereof ;

and wherein :

a, b, and d are integers with the following relationships ;

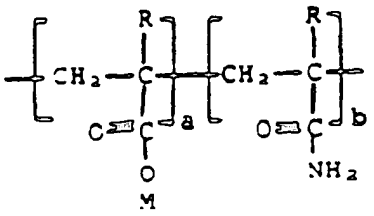
a/b = 0 to 100,

a/d = 0 to 100,

b/d = 0.01 to 100, and

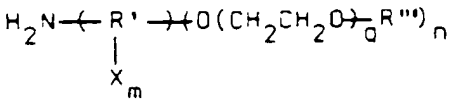
the ratio d : (a + b) is between 5 : 1 and 1 : 25, and wherein the occurrence of mer units of a, b, and d is random and the sum of a + b + d will achieve a molecular weight of at least 1000, preferably at least 2000, and most preferably between 1000 and 20,000,000 ; which process comprises reacting, in an aqueous solvent :

A. a polymer having pendant amide functional groups and represented by the structure :



wherein R, M, a, and b have the meanings above and wherein the sum of a + b achieves a molecular weight of at least 500 ; and

B. a chemical reactant having the structure :



wherein R', R‴, M, X, m, n and q have the meanings above ; under the following reaction conditions :

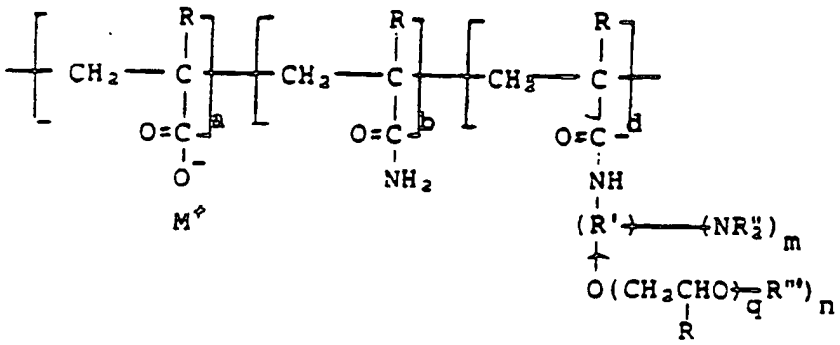
I. a reaction temperature of at least 100°C and preferably at least 110°C ;

II. a reaction time of at least 0.25 hour and preferably at least 0.5 hour ;

III. a mole ratio of chemical reactant to polymer ranging between 2 : 1 and 1 : 50 ;

IV. a pressure ranging from atmospheric pressure to 35 bar, or more ; thereby achieving the synthesis of the alkoxylated polymers described above, and then recovering the substituted/alkoxylated amide containing polymers.

It is particularly of interest that the synthetic procedures permit the synthesis of an alkoxylated polymer represented by :



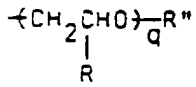
wherein :

R is hydrogen, methyl or ethyl ;

M is hydrogen, sodium, potassium, or ammonium or mixtures thereof ;

R′ is a linear or branched, multi-covalent alkylene bridging group having from 1 to 6 carbon atoms ;

R″ is a lower alkyl (C_1-C_4) group, or an alkoxylate group represented by



R‴ is hydrogen or a lower alkyl (C_1-C_4) group, and

m = 0 to 3 ;

n = 1 to 3 ;

q = 1 to 10 ; and

a, b and d are integers having the relationships ;

a/d = 0 to 50 ;

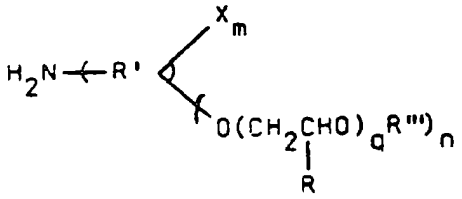
a/b = 0 to 50 ;

b/d = 0.1 to 20,

d : (a + b) = 5 : 1 to 1 : 10, and wherein

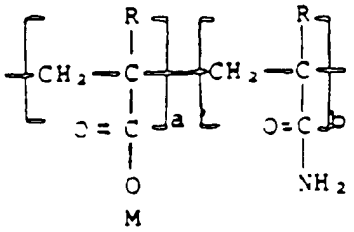
the sum of a + b + d is sufficient to provide a molecular weight of at least 1,000 ; which process comprises the reaction, in an aqueous solvent, for at least 0.1 hour at a temperature of at least 110°C, in a pressure controlling reactor, of the ingredients :

A. a reactant :

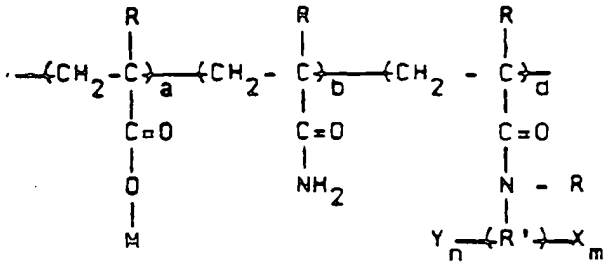


wherein R, R′, R‴,X, m, n and q have the above meanings ; and

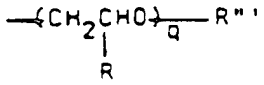
B. a water-soluble vinyl polymer having pendant amide groups represented by :



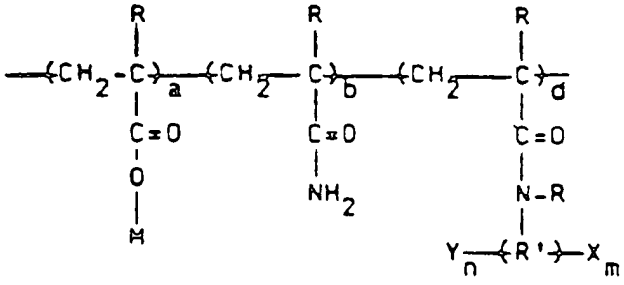
wherein R, M, a, and b have the above meanings ; and wherein the mole ratio of reactant to pendant amide groups ranges between 2 : 1 and 1 : 5 ;
and then recovering the alkoxylated polymer. Preferred embodiments of the water-soluble polymers according to the invention are the following :
Water-soluble polymers represented by :



wherein R' is a multivalent hydrocarbon bridging group having from 2-12 carbon atoms and being chosen from linear and branched alkyl, aryl, alkaryl, cyclic and heterocyclic groups, and mixtures thereof ; and where R" is a linear or branched alkyl, aryl, alkaryl, cyclic or heterocyclic hydrocarbon group having from 1 to 20 carbon atoms or an alkoxyl group represented by :

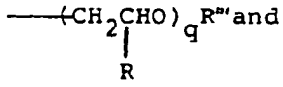


m = 0 to 10 ;
n = 1 to 10, provided the sum (m + n) = 1 to 12 ; and further
wherein (a + b + d), the sum, is sufficient to achieve a molecular weight of from 1,000 to 20,000,000, and M is H, a lower alkyl (C_1-C_4) group, an alkali metal or ammonium ion, or mixtures thereof.
Water-soluble polymers represented by :

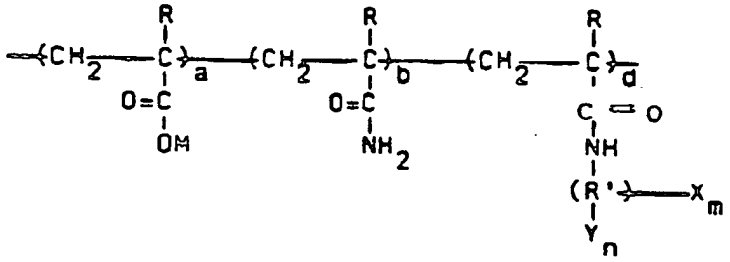


wherein
R is hydrogen or a lower alkyl (C_1-C_4) group ;
R' is a multivalent linear or branched alkyl, aromatic, cyclic, and/or heterocyclic bridging group having from 1 to 8 carbon atoms ; and

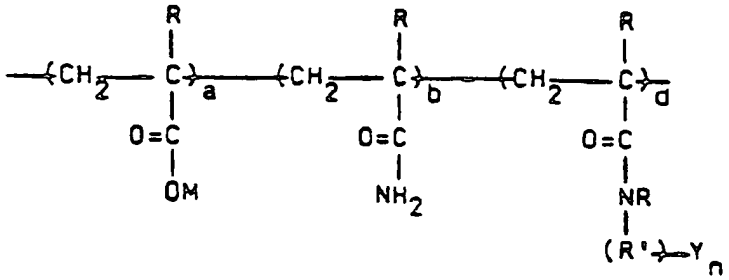
R" is a hydrocarbon substituent group having from 1-6 carbon atoms or an alkoxylate substituent represented by



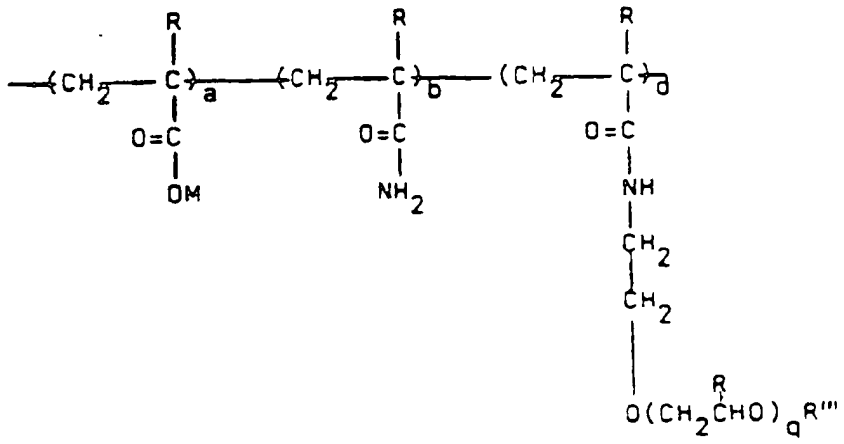
mixtures thereof, and
M is H, Li, Na, K, NH_4, or mixtures thereof ; and
n = 1 to 8 ;
m = 0 to 8, provided the sum, m + n = 1 – 10.
Water-soluble polymers wherein :
R is methyl, R' is a linear or branched alkyl, aromatic and/or cyclic group and when p is 1, the the gegenion is chloride, bromide, hydroxyl, and methylsulfate, and mixtures thereof ;
m = 0 to 4,
n = 1 to 4, provided m + n = 1 – 8 ;
(a + b)/d = 0.01 – 50 and
q = 1 to 25.
Water-soluble polymers represented by



wherein ;
R is hydrogen or methyl ;
R' is a linear or branched alkylene group having from 1 to 6 carbon atoms ;
M is H, Li, Na, K, NH_4, and mixtures thereof ;
m = 1 – 6,
n = 1 – 6, and
q = 1 – 30.
Polymers represented by :

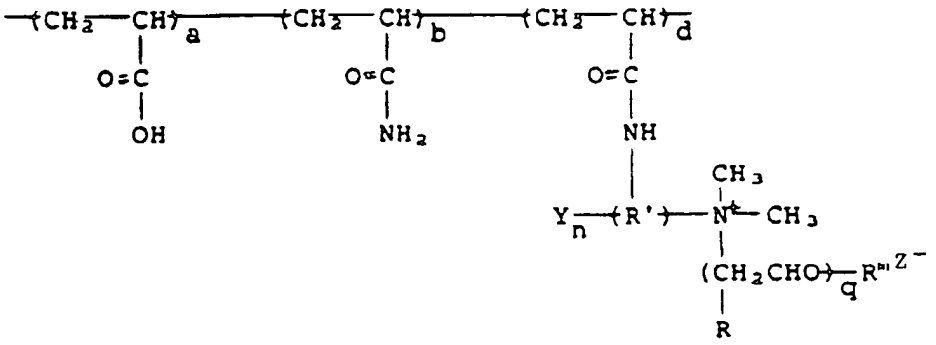


wherein
R is hydrogen or a lower alkyl (C_1-C_4) group ;
R' is a linear or branched alkylene group having from 1 to 6 carbon atoms ;
M is H, Li, Na, K, NH_4, and mixtures thereof ;
n = 1 – 6.
Polymers represented by :



wherein R is hydrogen or a lower alkyl group having from 1 to 4 carbon atoms ; and the sum, a + b + d, is sufficient to achieve a molecular weight of from 1,000-20,000,000.

Polymers represented by :



wherein

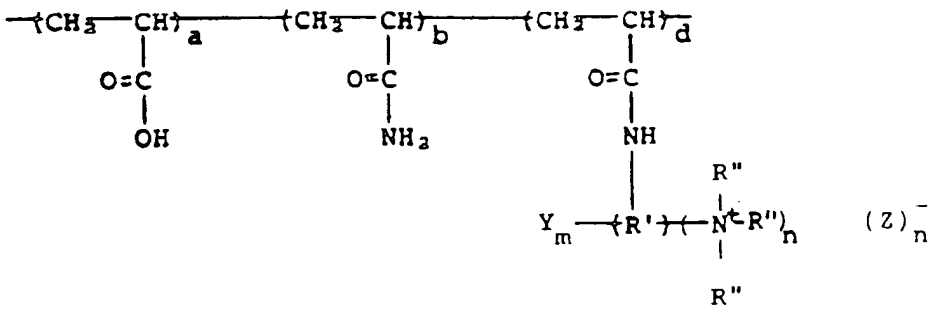
R' is a linear or branched, hydrocarbon group containing from 1 to 6 carbon atoms ; Z^- is Cl^-, Br^-, I^-, and mixtures thereof ;

R = H or a lower alkyl (C_1-C_4) group ;

q = 0 – 30 ; and

n = 1 – 6.

Polymers having a molecular weight of at least 1000, represented by .



wherein

R' is a linear or branched hydrocarbon group containing from 2-5 carbon atoms ; Z^- is Cl^-, Br^-, I^-, OH^-, methyl sulfate and mixtures thereof ;

R'' is methyl, ethyl, propyl, butyl and isomers thereof ;

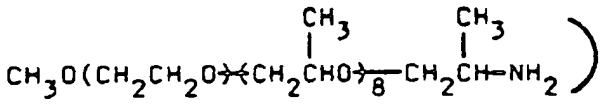
R''' is hydrogen and/or a lower alkyl (C_1-C_4) group ;

m = 0 to 4 ; and

n = 1 to 4.

Example I

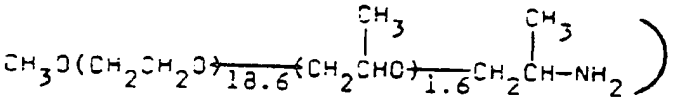
A mixture of poly [acrylic acid (25 mole percent) – acrylamide (75 mole percent)] (31.5% actives, 63 g), and Jeffamine M-600 (106.1 g) was heated in a 600 ml Parr reactor at 150°C for 7 hours. (Jeffamine M-600 is a trademark of Texaco Chemical Company and is used to describe a chemical reactant having primarily the chemical formula :



The product was characterized by L.C. and Cl3 NMR methods. L.C. analysis of the residual Jeffamine M-600 showed that 69.5% of the amine charged reacted and thus, the polymer contained 13.9 mole percent N-alkoxylated amide.

Example II

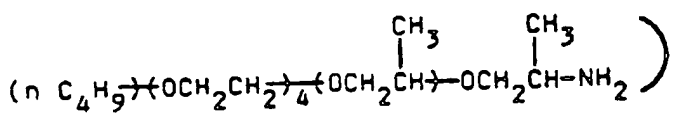
A mixture of poly [acrylic acid (25 mole percent) acrylamide (75 mole percent)] (31.5% actives, 80 g) and Jeffamine M-1000 (70.7 g) was heated in a 300 ml Parr reactor at 150°C for 7 hours. (Jeffamine M-1000 is a trademark of Texaco Chemical Company and is used to describe a chemical reactant having primarily the chemical formula :



The product was characterized by L.C. and Cl3 NMR methods. L.C. analysis of the residual Jeffamine M-1000 showed that 74.4% of the amine charged reacted and thus, the polymer contained 14.9 mole percent N-alkoxylated amide.

Example III

A mixture of poly [acrylic acid (25 mole percent) acrylamide (75 mole percent)] (31.5% actives, 129 g) and Jeffamine M-360 (41 g) was heated in a 300 ml Parr reactor at 150°C for 7 hours. (Jeffamine M-360 is a trademark of Texaco Chemical Company and is used to describe a chemical reactant having primarily the chemical formula :



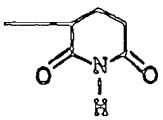
The product was charact rized by L.C. and Cl3 NMR methods. L.C. analysis of the residual Jeffamine M-360 showed that 56% of amine charged reacted and thus, the polymer contained 11 mole percent N-alkoxylated amide.

Example IV

A solution of poly [acrylic acid (25 mole percent) acrylamide (75 mole percent)] (27.5% actives, 150 g), 1-amino-2,3-propanediol (10.6 g) was heated in a 300 ml Parr reactor at 150°C for 4 hours. The product was characterized by L.C. and CI3 NMR methods. The molecular weight of the polymer was found to be 14,600. L.C. analysis of the residual 1-amino-2,3-propanediol showed that 92% of the amine charged reacted and thus, the polymer contained 18.6 mole percent N-(2,3 dihydroxy) propylamide.

Example V

A solution of poly [acrylic acid (50 mole percent) acrylamide (50 mole percent)] (31.5% actives, 150 g), 1-amino-2,3-propanediol (12 g) was heated in a 300 ml Parr reactor at 150°C for 4 hours. The product was characterized by L.C. and CI3 NMR methods. The molecular weight of the polymer was found to be 76,600. L.C. analysis of the residual 1-amino-2,3-propanediol showed that 92% of the amine charged reacted. The composition of the polymer was estimated to be 50 mole percent acrylate, 25 mole percent acrylamide, 18.3 mole percent N-(2,3-dihydroxy) propylamide, and 6.7 mole percent of a cyclic amide, represented by the structure :



Example VI

A solution of poly [acrylic acid (25 mole percent) acrylamide (75 mole percent)] (27.5% actives, 150 g), tris(hydroxy methyl) amino methane (14 g) was heated in a 300 ml Parr reactor at 150°C for 4 hours. The product was characterized by L.C. and CI3 NMR methods. The molecular weight of the polymer was found to be 11,600. L.C. analysis of the residual tris(hydroxy methyl) amino methane showed that only 14% of the amine charged reacted and thus, the polymer contained about 3 mole percent of the secondary amide.

Example VII

A solution of poly [acrylic acid (50 mole percent) acrylamide (50 mole percent)] (31.5% actives, 150 g) 2-amino-2-methyl-1,3-propandiol (13.9 g) was heated at 150°C in a 300 ml Parr reactor for 4 hours. The product was characterized by L.C. and CI3 NMR methods. The molecular weight of the polymer was found to be 16,000. Residual amine was determined by L.C. methods. The composition of the polymer was estimated to be 75 mole percent acrylate, 15 mole percent acrylamide, 3 mole percent secondary amide, and 7 mole percent cyclic imide.

Example VIII

The reaction conditions were similar to those employed in Example I. In this particular case, the finished polymer contained 7.6 mole percent of the acrylamide groups converted to the N-(1,1-dimethyl-2-hydroxyethyl) acrylamide groups.

In addition, the following polymer could be synthesized if acrylamide containing polymers were reacted according to the procedures described above with the following chemical reactants : The anticipated products are described in Table I. In this table, AA means acrylic acid mer unit (or its salts or esters) ; AcAm means acrylamide mer units, and a, b and d have the meanings above. T indicates any terminal end group from any free radical catalyst, or from any reaction which would lead to deactivation of a polymer propagating radical, such reaction being disproportionation, hydrogen abstraction, coupling, and the like.

TABLE I

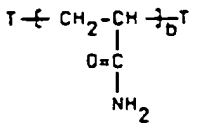
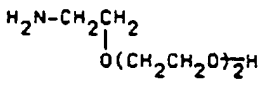
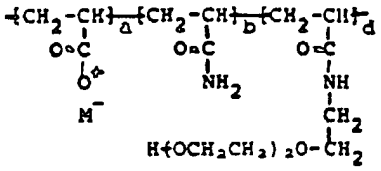
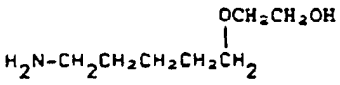
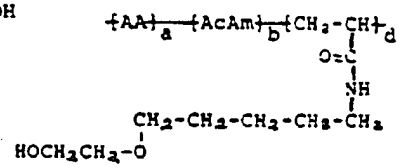
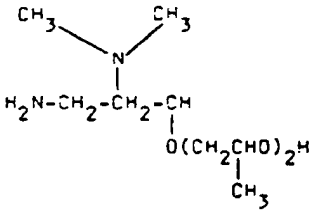
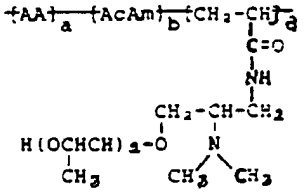
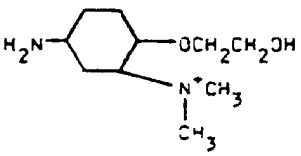
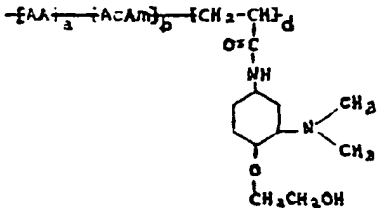
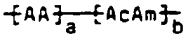
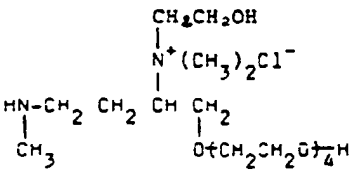
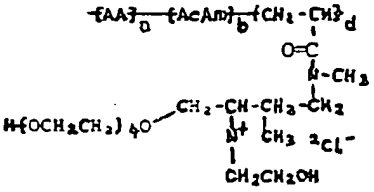
Starting Polymer	Starting Chemical Reactant	Anticipated Product Polymer
		
"		
"		
"		
		

TABLE I

(Continued)

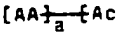
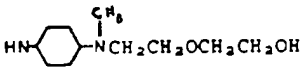
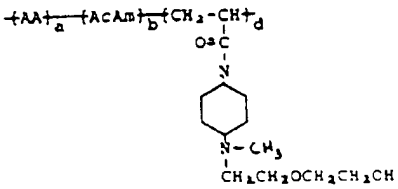
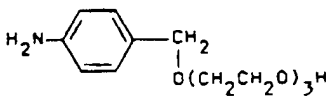
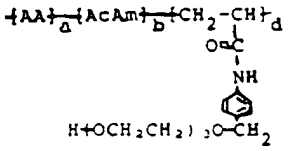
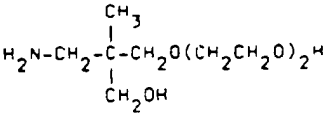
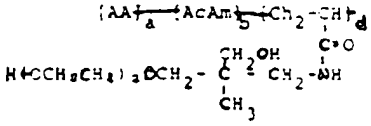
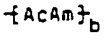
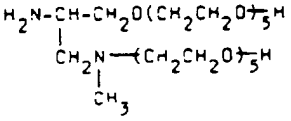
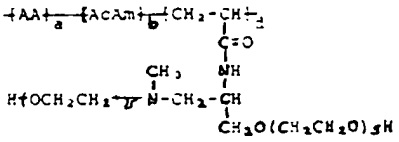
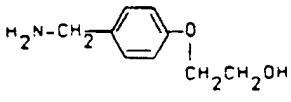
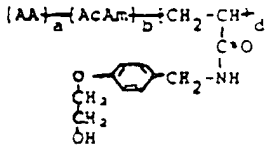
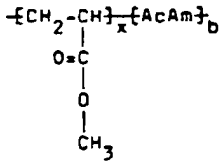
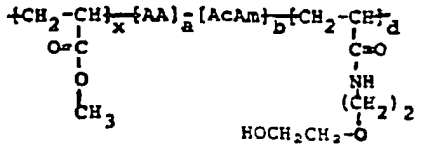
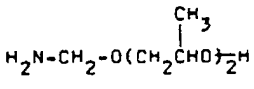
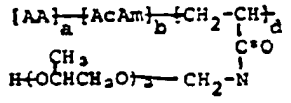
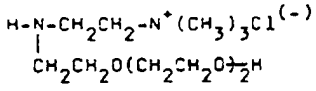
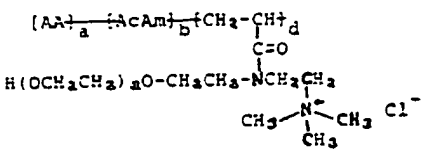
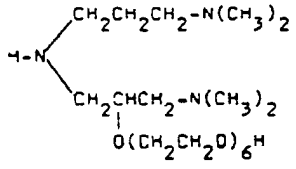
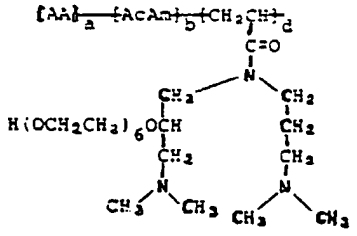
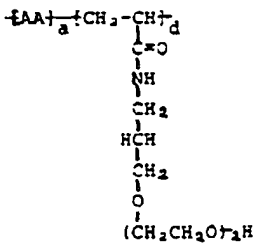
Starting Polymer	Starting Chemical Reactant	Anticipated Product Polymer
		
		
		
		
		

TABLE I

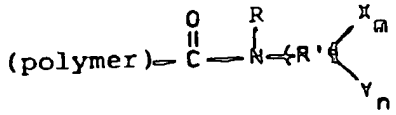
(Continued)

Starting Polymer	Starting Chemical Reactant	Anticipated Product Polymer
	$H_2N-CH_2CH_2OCH_2CH_2OH$	
$+AcAm+$		
$+AcAm+_b$		
$+AcAm+_b$		
$+AA+_a+AcAm+_b$	$H_2NCH_2-CH_2-CH_2$ $O(CH_2CH_2O)_2H$	

Claims

Claims for the Contracting States : BE, CH, DE, FR, GB, GR, IT, LI, NL, SE

1. Water-soluble pendant substituted amide containing polymers having a molecular weight of at least 500 which have at least 1 mole percent of their original pendant amide groups converted to pendant substituted amide structures represented by :

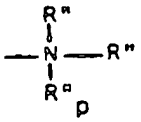


wherein :

R is chosen, at each occurrence, from hydrogen or a lower alkyl (C_1-C_4) group

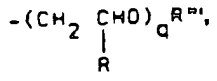
R' is a multivalent hydrocarbon bridging group having from 1-20 carbon atoms and which may be linear or branched alkyl ; aryl ; alkaryl, cyclic, heterocyclic, and mixtures thereof ;

X is represented by the formula :



wherein

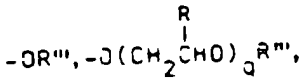
R" is a hydrocarbon group chosen, at each occurrence, from linear or branched alkyl, aryl, alkaryl, cyclic, heterocyclic, or 2 R" groups taken together to form a ring, alkoxyl groups represented by



and mixtures thereof, and

R"' is individually chosen, at each occurrence, from hydrogen, or hydrocarbon groups having from 1 to 20 carbon atoms and being linear or branched alkyl groups, aryl and alkaryl, cyclic and heterocyclic groups, and mixtures thereof ;

Y is chosen, at each occurrence, from the group consisting of



and mixtures thereof ; and

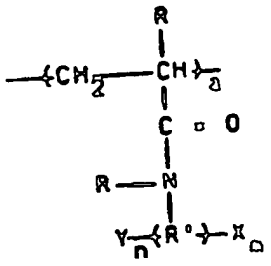
m = 0 – 20 and

n = 1 – 20,

p is from 0 to 1, provided that when p is 1, an electroneutralizing gegenion is equivalently present ;

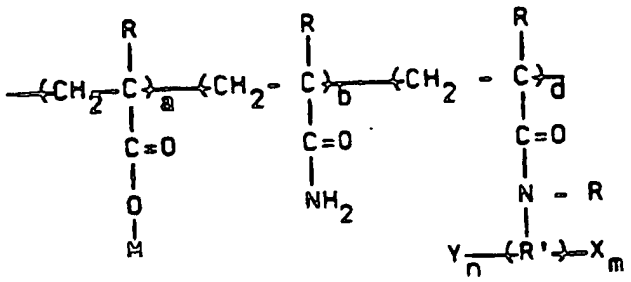
q = 1 – 50.

2. The water-soluble acrylamide polymers of claim 1 having a molecular weight of at least 500 which have at least 1 mole percent of their original acrylamide mer units converted to a structure :



wherein X, Y, R, R', n, and m have the same meanings as in Claim 1, and a is at least 10.

3. The water-soluble acrylamide polymers of claim 1 which have at least 1 mole percent of their original acrylamide mer units converted to a structure :



wherein X, Y, R, R', n, and m have the same meanings as in claim 1,

M is chosen, at each occurrence, from the group consisting of hydrogen, lower alkyl (C_1-C_4) groups, alkali metals, alkaline earth metals, ammonium, primary secondary, and tertiary amines, and quaternary ammonium groups, and mixtures thereof ; and wherein

a is at least 10 and

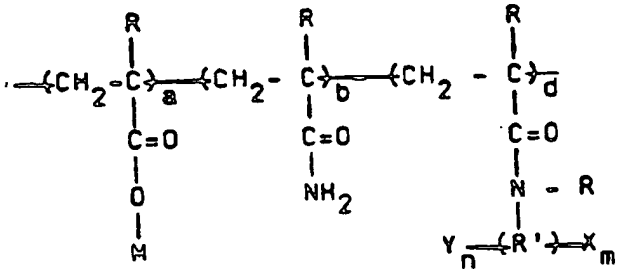
(a + b + d), the sum, is sufficient to achieve a molecular weight of at least 500 ;

and wherein the following relations exist :

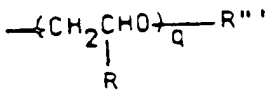
a/b	=	up to 100 ;
a/d	=	up to 100 ;
(a + b)/d	=	0.01 to 100 ; and
b/d	=	0,01 to 100,

and wherein each mer unit defined by a, b, or d is randomly distributed within the polymer.

4. The water-soluble polymers of claim 3 represented by :

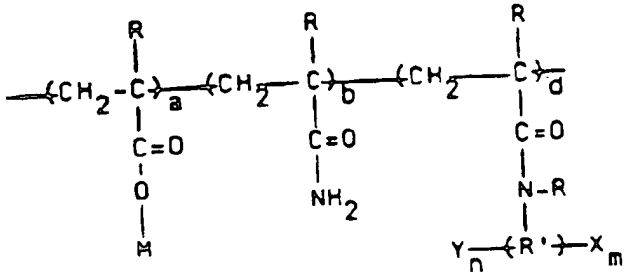


wherein R' is a multivalent hydrocarbon bridging group having from 2-12 carbon atoms and being chosen from linear and branched alkyl, aryl, alkaryl, cyclic and heterocyclic groups, and mixtures thereof ; and where R" is a linear or branched alkyl, aryl, alkaryl, cyclic or heterocyclic hydrocarbon group having from 1 to 20 carbon atoms or an alkoxyl group represented by :

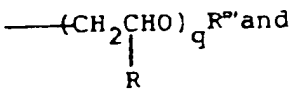


m = 0 to 10 ;
n = 1 to 10, provided the sum (m + n) = 1 to 12 ; and further
wherein (a + b + d), the sum, is sufficient to achieve a molecular weight of from 1,000 to 20,000,000, and
M is H, a lower alkyl (C_1-C_4) group, an alkali metal or ammonium ion, or mixtures thereof.

5. The water-soluble polymers of claims 3 or 4 represented by :



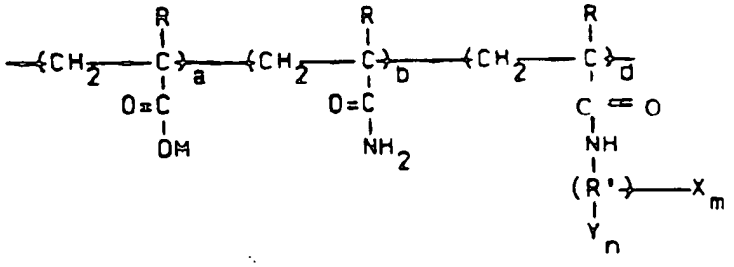
wherein
R is hydrogen or a lower alkyl (C_1-C_4) group ;
R′ is a multivalent linear or branched alkyl, aromatic, cyclic, and/or heterocyclic bridging group having from 1 to 8 carbon atoms ; and
R″ is a hydrocarbon substituent group having from 1-6 carbon atoms or an alkoxylate substituent represented by



mixtures thereof, and
M is H, Li, Na, K, NH_4, or mixtures thereof ; and
n = 1 to 8 ;
m = 0 to 8, provided the sum, m + n = 1 – 10,

6. The water-soluble polymers of claim 5 wherein :
R is methyl, R′ is a linear or branched alkyl, aromatic and/or cyclic group and when p is 1, the the gegenion is chloride, bromide, hydroxyl, and methylsulfate, and mixtures thereof ;
m = 0 to 4,
n = 1 to 4, provided m + n = 1 – 8 ;
(a + b)/d = 0.01 – 50 and
q = 1 to 25.

7. The water-soluble polymers of claims 4 or 5, represented by



wherein ;

R is hydrogen or methyl ;

R' is a linear or branched alkylene group having from 1 to 6 carbon atoms ;

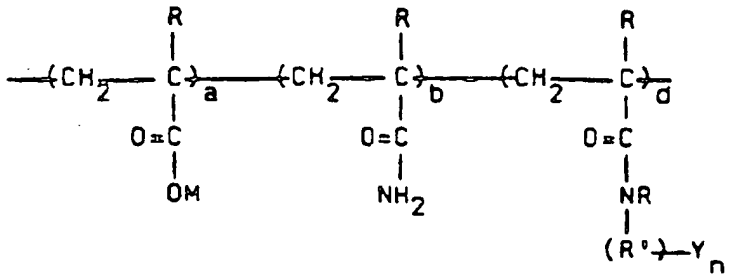
M is H, Li, Na, K, NH_4, and mixtures thereof ;

m = 1 – 6,

n = 1 – 6, and

q = 1 – 30.

8. The polymers of claim 3 represented by :



wherein

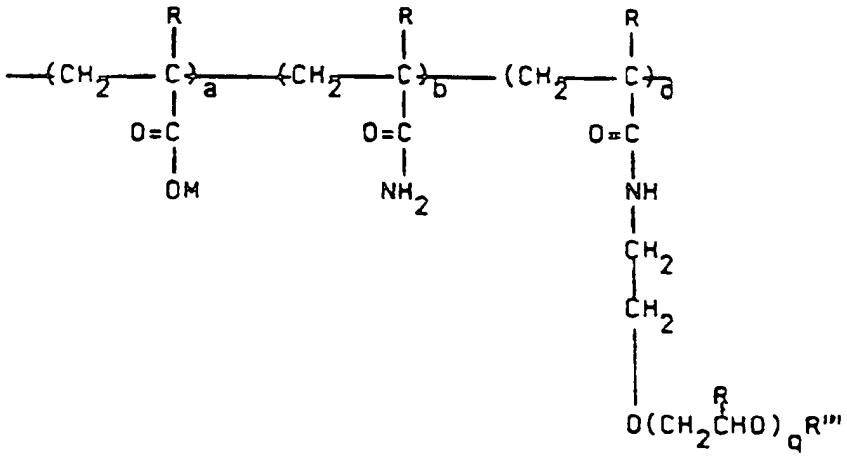
R is hydrogen or a lower alkyl (C_1-C_4) group ;

R' is a linear or branched alkylene group having from 1 to 6 carbon atoms ;

M is H, Li, Na, K, NH_4, and mixtures thereof ;

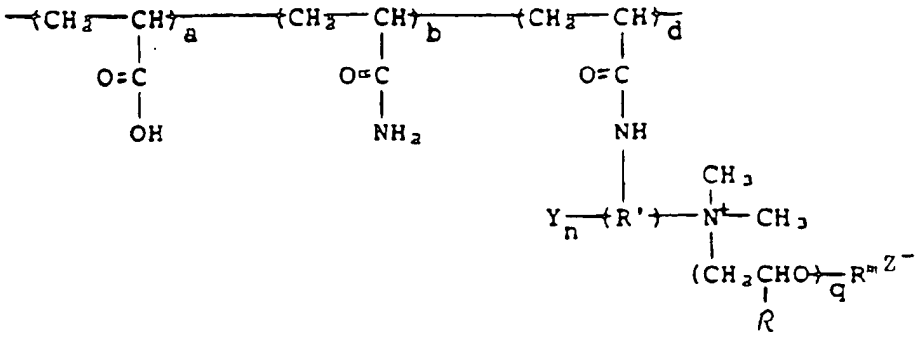
n = 1 – 6.

9. The polymers of claim 8 represented by :



wherein R is hydrogen or a lower alkyl group having from 1 to 4 carbon atoms ; and the sum, a + b + d, is sufficient to achieve a molecular weight of from 1,000-20,000,000.

10. The polymers of claim 7, represented by :



wherein

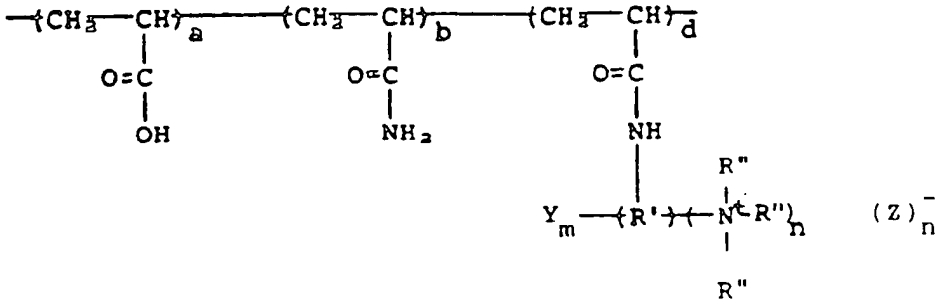
R′ is a linear or branched, hydrocarbon group containing from 1 to 6 carbon atoms ; Z^- is Cl^-, Br^-, I^-, and mixtures thereof ;

R = H or a lower alkyl (C_1-C_4) group ;

q = 0 – 30 ; and

n = 1 – 6.

11. The polymers of claim 7 having a molecular weight of at least 1000, represented by :



wherein

R′ is a linear or branched hydrocarbon group containing from 2-5 carbon atoms ; Z^- is Cl^-, Br^-, I^-, OH^-, methyl sulfate and mixtures thereof ;

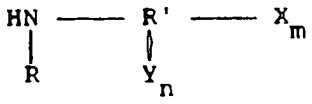
R″ is methyl, ethyl, propyl, butyl and isomers thereof ;

R‴ is hydrogen and/or a lower alkyl (C_1-C_4) group ;

m = 0 to 4 ; and

n = 1 to 4.

12. A process for producing the polymers of claim 1 to 11 by transamidation of a polymer/copolymer containing pendant amide functional groups with a chemical reactant of the formula :



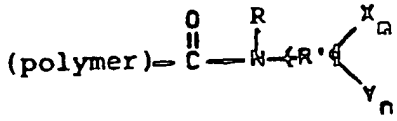
wherein the substituents and indices have the same meanings as in claims 1 to 11.

13. The use of the polymers of claims 1 to 11 in water treatment such as dispersants, scale inhibitors, flocculants, coagulants or thickeners.

Claims for the Contracting States : AT and ES

1. A process for producing water-soluble pendant substituted amide containing polymers having a molecu-

lar weight of at least 500 which have at least 1 mole percent of their original pendant amide groups converted to pendant substituted amide structures represented by :

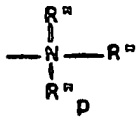


wherein :

R is chosen, at each occurrence, from hydrogen or a lower alkyl (C_1-C_4) group

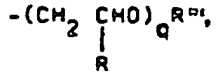
R' is a multivalent hydrocarbon bridging group having from 1-20 carbon atoms and which may be linear or branched alkyl ; aryl ; alkaryl, cyclic, heterocyclic, and mixtures thereof ;

X is represented by the formula :



wherein

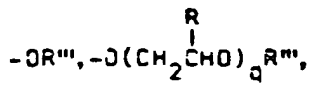
R" is a hydrocarbon group chosen, at each occurrence, from linear or branched alkyl, aryl, alkaryl, cyclic, heterocyclic, or 2 R" groups taken together to form a ring, alkoxyl groups represented by



and mixtures thereof, and

R"' is individually chosen, at each occurrence, from hydrogen, or hydrocarbon groups having from 1 to 20 carbon atoms and being linear or branched alkyl groups, aryl and alkaryl, and cyclic groups, and mixtures thereof ;

Y is chosen, at each occurrence, from the group consisting of



and mixtures thereof ; and

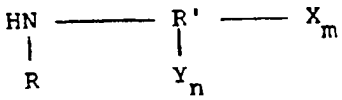
m = 0 – 20 and

n = 1 – 20,

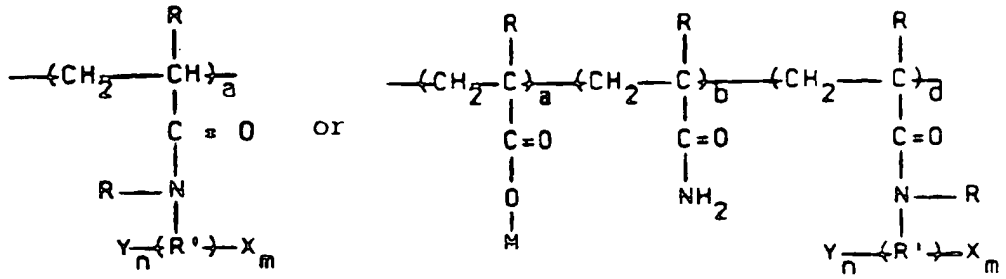
p is from 0 to 1, provided that when p is 1, an electroneutralizing gegenion is equivalently present ;

q = 1 – 50

by transamidation reaction of a polymer/copolymer containing amide functional groups with a chemical reactant of the formula :



2. The process of claim 1 for producing polymers having at least 1 mole-% of their original acrylamide units converted to units of the formula :



wherein the substituents and indices have the same meaning as in claim 1 and M is H, a C_1 to C_4 alkyl group, an alkali or alkaline earth metal, an ammonium or quaternary ammonium group or a primary, secondary or tertiary amine ;

a ≧10

a + b + d is sufficient to achieve a molecular weight of at least 500 and

a/b = up to 100 ;

a/d = up to 100 ;

(a + b)/d = 0.01 – 100 ; and

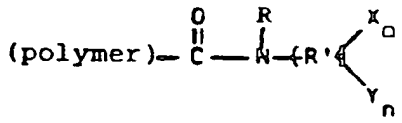
b/d = 0.01 – 100

and wherein the units are randomly distributed within the polymer.

Ansprüche

Patentansprüche für die Vertragsstaaten : BE, CH, DE, FR, GB, GR, IT, NL, SE

1. Wasserlösliche Polymere mit substituierten Amid-Seitenketten und einem Molekulargewicht von zumindest 500, bei denen zumindest 1 Mol-% der ursprünglichen Amidgruppen umgewandelt sind in substituierte Amidstrukturen der Formel

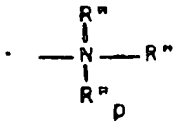


worin

R jeweils Wasserstoff oder eine niedere C_1-C_4-Alkylgruppe,

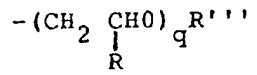
R' eine mehrwertige Kohlenwasserstoff-Brückengruppe mit 1 bis 20 Kohlenstoffatomen ist, die eine lineare oder verzweigte Alkylgruppe, eine Aryl-, Alkaryl-, cyclische oder heterocyclische Gruppe oder deren Gemische sein kann,

X der Formel

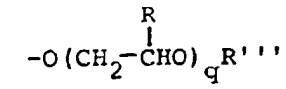


entspricht, worin

R" eine Kohlenwasserstoffgrupppe in Form einer linearen oder verzweigten Alkylgruppe, einer Aryl-, Alkaryl-, cyclischen oder heterocyclischen Gruppe sein kann und 2 R"-Substituenten zusammen einen Ring zu bilden vermögen, Alkoxygruyyen der Formel

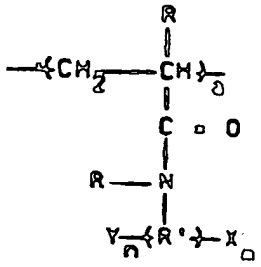


oder deren Gemische,
worin
R''' ein Wasserstoffatom oder eine C_1-C_{20}-Kohlenwasserstoffgruppe sein kann, die ihrerseits eine lineare oder verzweigte Alkylgruyye, Aryl- oder Alkaryl-, cyclische oder heterocyclische Gruppe oder deren Gemische ist, und
Y eine Gruppierung-OR''' und/oder



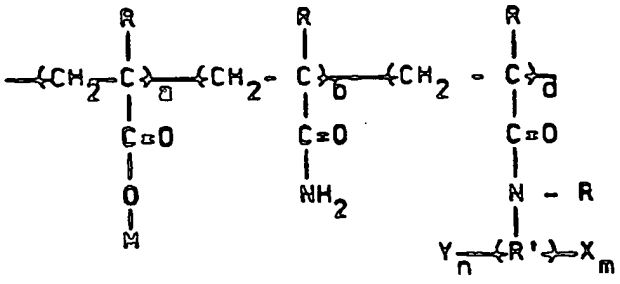
ist, in welcher
m = 0 – 20
n = 1 – 20
p 0 bis 1 sein kann mit der Maßgabe, daß, wenn p 1 ist, ein elektroneutralisierendes Gegenion äquivalent vorhanden ist und q 1-50 beträgt.

2. Wasserlösliches Acrylamidpolymer nach Anspruch 1 mit einem Molekulargewicht von zumindest 500 und zumindest 1 Mol-% der ursprünglichen Acrylamideinheiten umgesetzt sind in eine Struktur



worin X, Y, R, R', n und m die in Anspruch 1 angegebene Bedeutung haben und a zumindest 10 beträgt.

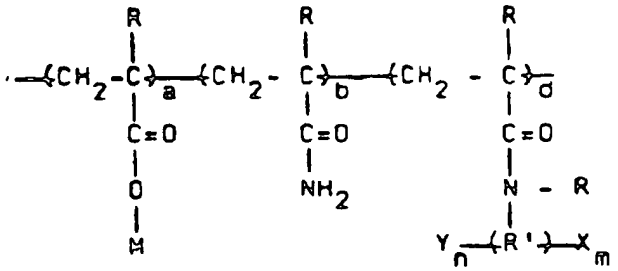
3. Wasserlösliche Acrylamidpolymere nach Anspruch 1, bei denen zumindest 1 Mol-% der ursprünglichen Acrylamideinheiten umgesetzt sind in eine Struktur



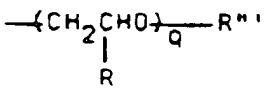
worin X, Y, R, R', n und m die in Anspruch 1 angegebene Bedeutung haben und
M ein Wasserstoffatom, eine niedere C_1-C_4-Alkylgruppe, ein Alkalimetall, Erdalkalimetall, Ammoniumgruppe, primäre, sekundär oder tertiäre Aminogruppe, eine quaternäre Ammoniumgruppe oder deren Gemische bedeuten kann und worin
a zumindest 10 beträgt und die Summe a + b + d ausreicht für ein Molekulargewicht von zumindest 500 und folgend B ziehungen bestehen :
a/b = bis zu 100 ;
a/d = bis zu 100 ;

(a + b)/d = 0,01 bis 100 ; und
b/d = 0,01 bis 100,
und die durch a, b oder d definierten Einheiten innerhalb des Polymeren regellos verteilt sind.

4. Wasserlösliche Polymere nach Anspruch 3 der Formel :

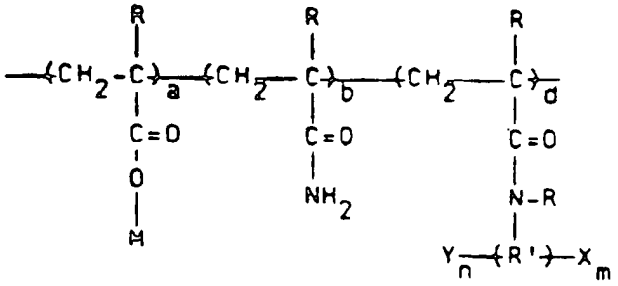


worin R' eine mehrwertige Kohlenwasserstoffgruppe mit 2-12 Kohlenstoffatomen in Form einer linearen oder verzweigten Alkylgruppe, einer Aryl-, Alkaryl-, cyclischen oder heterocyclischen Gruppe oder deren Gemische bedeutet und R" eine gerade oder verzweigte Alkylgruppe, eine Aryl-, Alkaryl-, cyclische oder heterocyclische Kohlenwasserstoffgruppe mit 1-20 Kohlenstoffatomen oder eine Alkoxygruppe der Formel :

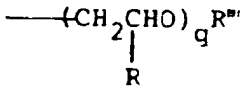


ist, worin
m = 0 bis 10 ;
n = 1 bis 10 sein kann, vorausgesetzt daß die Summe (m + n) 1 bis 12 beträgt ;
die Summe (a + b + d) ausreicht für ein Molekulargewicht von 1000 bis 20000000 und M = H, eine niedere C_1-C_4-Alkylgruppe, ein Alkalimetall oder ein Ammoniumion oder deren Gemische sein kann.

5. Wasserlösliches Polymer nach Anspruch 3 oder 4 der Formel :



worin
R ein Wasserstoffatom oder eine niedere C_1-C_4-Alkylgruppe ;
R' eine mehrwertige lineare oder verzweigte Alkylgruppe, eine Aryl-, cyclische und/oder heterocyclische Brückengruppe mit 1-8 Kohlenstoffatomen und
R" eine Kohlenwasserstoffgruppe mit 1-6 Kohlenstoffatomen oder eine Alkoxylatgruppe der Formel

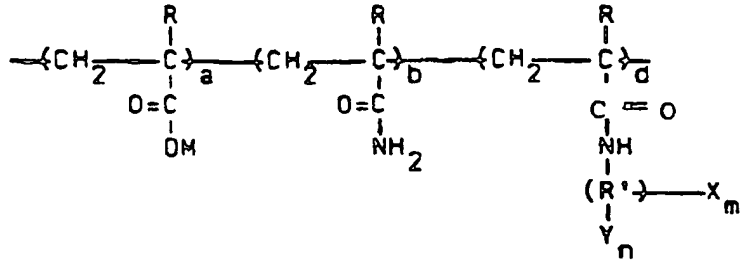


oder deren Gemische ist, wobei

M H, Li, Na, K, NH_4 oder deren Gemische bedeutet und
n 1 bis 8 und
m 0 bis 8 sein können, mit der Maßgabe, daß die Summe
m + n 1 bis 10 beträgt.

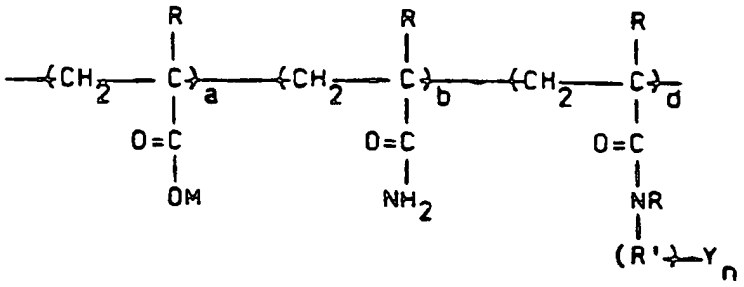
6. Wasserlösliche Polymere nach Anspruch 5, wobei R Methyl, R' eine gerade oder verzweigte Alkyl-, Aryl- und/oder cyclische Gruppe und p 1 ist, das Gegenion ein Chlorid, Bromid, Hydroxyl und/oder Methylsulfat sein kann ;
m 0 bis 4,
n 1 bis 4 ist mit der Maßgabe, daß m + n 1-8 beträgt,
(a + b)/d 0,01 – 50 und
q 1 bis 25 ist.

7. Wasserlösliche Polymere nach Anspruch 4 oder 5 der Formel :



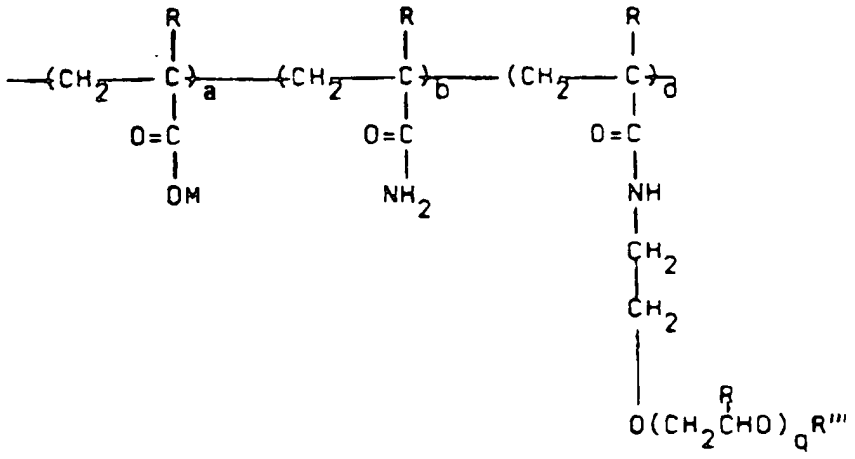
worin
R Wasserstoff oder Methyl ;
R' eine lineare oder verzweigte Alkylengruppe mit 1-6 Kohlenstoffatomen ;
M H, Li, Na, K, NH_4 oder deren Gemische sein kann ;
und
m 1 bis 6,
n 1 bis 6 und
q 1 – 30 ist.

8. Polymere nach Anspruch 3 der Formel :



worin
R ein Wasserstoffatom oder eine niedere C_1-C_4-Alkylgruppe ;
R' eine lineare oder verzweigte Alkylengruppe mit 1 bis 6 Kohlenstoffatomen ;
M H, Li, Na, K, NH_4 oder deren Gemische bedeuten kann und
n 1 bis 6 ist.

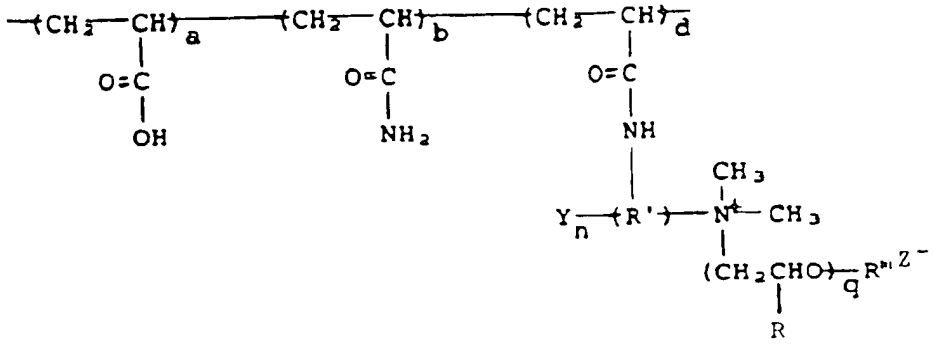
9. Polymere nach Anspruch 8 der Formel :



worin

R ein Wasserstoffatom oder eine niedere Alkylgruppe mit 1 bis 4 Kohlenstoffatomen ist und die Summe a + b + d ausreicht für ein Molekulargewicht von 1000 bis 20000000.

10. Polymere nach Anspruch 7 der Formel :



worin

R' eine lineare oder verzweigte Kohlenwasserstoffgruppe mit 1 bis 6 Kohlenstoffatomen ;

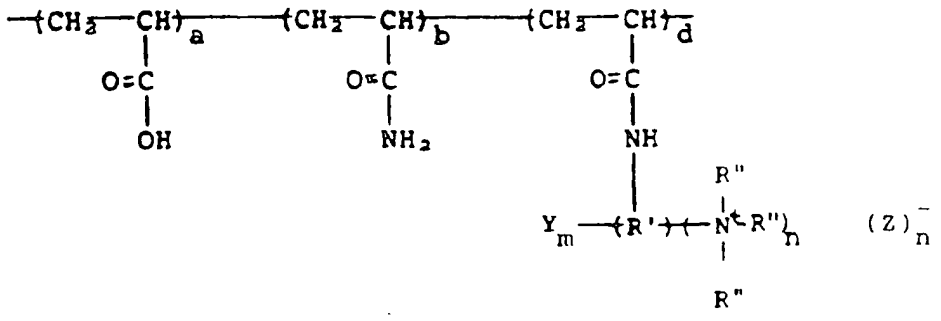
Z^- Cl^-, Br^-, I^- oder deren Gemische sein kann ;

R H oder eine niedere C_1-C_4-Alkylgruppe ist und

q 0 – 30 und

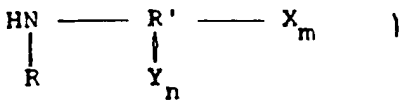
n 1 – 6 bedeuten.

11. Polymere nach Anspruch 7 mit einem Molekulargewicht von zumindest 1000 der Formel :



worin
R' eine lineare oder verzweigte Kohlenwasserstoffgruppe mit 2-5 Kohlenstoffatomen ;
Z^- Cl^-, Br^-, I^-, OH^-, Methylsulfat oder deren Gemische bedeutet ;
R'' Methyl, Ethyl, Propyl, Butyl und dessen Isomere ist und
R''' ein Wasserstoffatom und/oder eine niedere C_1-C_4-Alkylgruppe bedeutet ;
m 0 bis 4 und
n 1 bis 4 ist.

12. Verfahren zur Herstellung der Polymere nach Anspruch 1 bis 11 durch Transamidierung eines Polymeren oder Copolymeren enthaltend in einer Seitenkette funktionelle Aminogruppen mit einem Reaktionspartner der Formel :

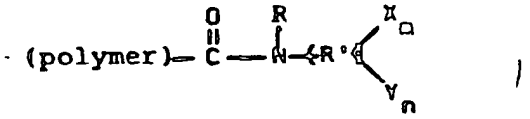


wobei die Substituenten und Indices die in den Ansprüchen 1 bis 11 angegebenen Bedeutungen haben.

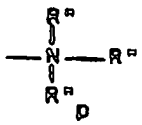
13. Anwendung der Polymere nach Anspruch 1 bis 11 zur Wasseraufbereitung wie als Dispersionsmittel, Korrosionsinhibitoren, Flockungsmittel, Koagulantien oder Eindicker.

Patentansprüche für die Vertragsstaaten : AT, ES

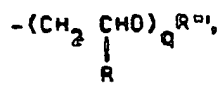
1. Verfahren zur Herstellung wasserlöslicher Polymerer enthaltend substituierte Aminogruppen in der Seitenkette mit einem Molekulargewicht von zumindest 500, bei denen zumindest 1 Mol-% der ursprünglichen Aminogruppen umgesetzt sind in substituierte Strukturen der Formel :



worin
R ein Wasserstoffatom oder eine niedere C_1-C_4-Alkylgruppe ;
R' eine mehrwertige Kohlenwasserstoff-Brückengruppe mit 1-20 Kohlenstoffatomen in Form einer linearen oder verzweigten Alkylgruppe, Aryl-, Alkaryl-, cyclischen oder heterocyclischen Gruppe oder deren Gemische sein kann ;
X der Formel :

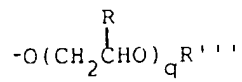


entspricht, worin
R'' eine Kohlenwasserstoffgruppe in Form einer linearen oder verzweigten Alkylgruppe, Aryl-, Alkaryl-, cyclischen oder heterocyclischen Gruppe ist oder 2 R''-Gruppen zusammen einen Ring bilden können, Alkoxygruppen der Formel

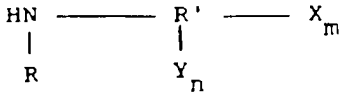


und deren Gemische und
R''' ein Wasserstoffatom oder eine Kohlenwasserstoffgruppe mit 1-20 Kohlenstoffatomen in Form von linearen oder verzweigten Alkylgruppen, Aryl- und Alkaryl- und cyclischen Gruppen und deren Gemischen

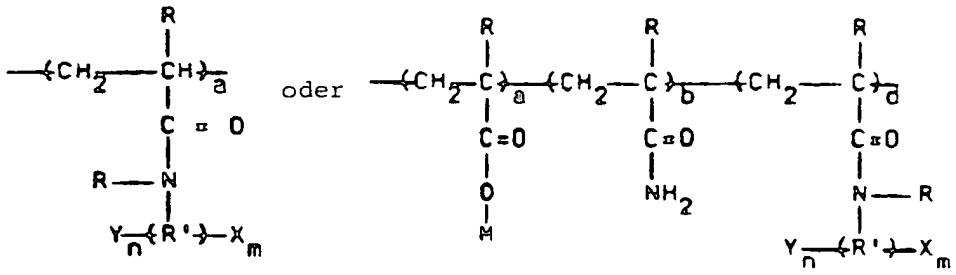
bedeuten kann und
Y-OR''' und/oder



ist, wobei
m 0 bis 20 und
n 1 bis 20
p 0 bis 1 sein können mit der Maßgabe, daß, wenn p 1 ist, ein elektroneutralisierendes Gegenion äquivalent vorhanden ist und
q 1 – 50 bedeutet,
durch Transamidierung eines Polymeren oder Copolymeren enthaltend funktionelle Aminogruppen mit einem Reaktionspartner der Formel :



2. Verfahren nach Anspruch 1 zur Herstellung von Polymeren, bei denen zumindest 1 Mol-% ihrer ursprünglichen Acrylamideinheiten umgewandelt sind in Einheiten der Formel :

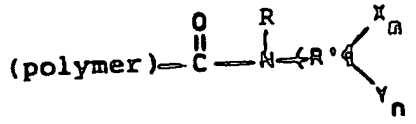


wobei die Substituenten und Indices die in Anspruch 1 angegebenen Bedeutungen haben und M H, eine C_1-C_4-Alkylgruppe, ein Alkali- oder Erdalkalimetall, eine Ammonium-oder quaternäre Ammoniumgruppe oder ein primäres, sekundäres oder tertiäres Amin sein kann ;
a ≧10,
a + b + d ausreichend hoch ist für ein Molekulargewicht von zumindest 500 ;
a/b bis zu 100 ;
a/d bis zu 100 ;
(a + b)/d 0,01 – 100 und
b/d 0,01 – 100
beträgt, wobei die Einheiten innerhalb des Polymeren regellos verteilt sind.

Revendications

Revendications pour Les Etats Contractants : BE, CH, DE, FR, GB, GR, IT, LI, NL, SE

1. Polymères solubles dans l'eau contenant des amides substitués, ayant un poids moléculaire d'au moins 500, lesquels ont au moins une mole pour cent de leurs groupements amides originaux convertis en une structure d'amides substitués représentées par :

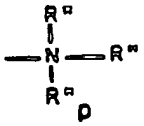


pour laquelle

R est choisi, pour chaque cas, parmi l'hydrogène ou un groupement alkyle inférieur (C_1-C_4)

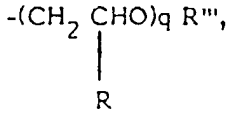
R' est un groupement de liaison hydrocarboné multtivalent ayant de 1 à 20 atomes de carbone et qui peut être un alkyle linéaire ou ramifié, un aryle, un alkaryle, un cycle ou un hétérocycle et leurs mélanges ;

X est présenté par la formule :



pour laquelle

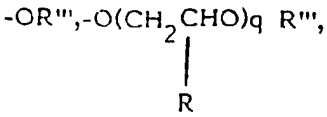
R" est un groupement hydrocarboné choisi pour chaque cas, parmi les groupements alkyles linéaires ou ramifiés, aryles, alkaryles, cycliques, hétérocycliques, ou deux groupements R" pris ensemble pour former un cycle, les groupements alkoxyles représentés par



et leurs mélanges, et

R"' est individuellement choisi, pour chaque cas, parmi l'hydrogène, un groupement hydrocarboné ayant de 1 à 20 atomes de carbone et étant des groupements alkyles linéaires ou ramifiés, aryles et alkiaryles, des groupements cycliques et hétérocycliques et leurs mélanges ;

Y est choisi, pour chaque cas, parmi le groupe consistant en



et leurs mélanges, et

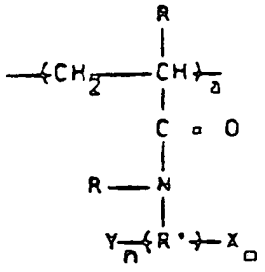
m = 0 – 20 et

n = 1 – 20,

p est de 0 à 1, prévoyant que lorsque p est 1, un ion complémentaire électroneutralisant est présent en équivalence ;

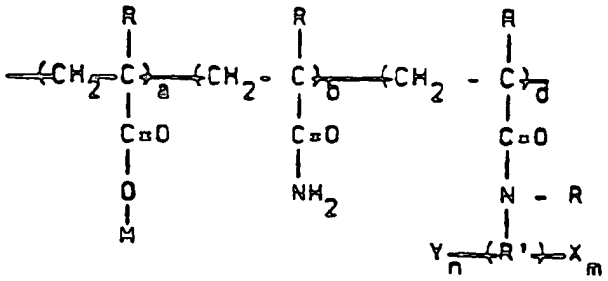
q = 1 – 50.

2. Les polymères acrylamides solubles dans l'eau selon la revendication 1, ayant un poid moléculaire d'au moins 500 lesquels ont au moins une mole pour 100 de leurs unités acrylamides originales converties en une structure :



pour laquelle X, Y, R, R', n et m ont la même signification que dans la revendication 1, et a est au moins 10.

3. Les polymères (métha)crylamides solubles dans l'eau selon la revendication 1, lesquels ont au moins une mole pour cent de leurs unités (meth)acrylamides originales converties en une structure :



pour laquelle X, Y, R, R', n et m ont la même signification que dans la revendication 1,

M est choisi, pour chaque cas, parmi le groupe consistant en l'hydrogène, les groupements alkyles inférieurs (C_1-C_4), les métaux alcalins, les métaux alkalino-terreux, l'ammonium, les amines primaires, secondaires et tertiaires, et les groupements ammoniums quaternaires, et leurs mélanges ;

et pour laquelle,

a est au moins 10 et

(a + b + d), la somme, est suffisante pour obtenir un poid moléculaire d'au moins 500 et pour laquelle les relations suivantes existent :

a/b = jusqu'à 100 ;

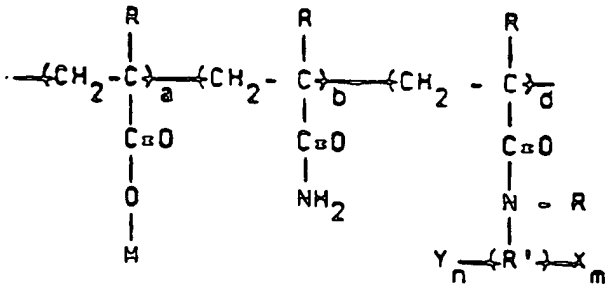
a/d = jusqu'à 100 ;

(a + b)/d = 0,01 à 100 ; et

b/d = 0,01 à 100,

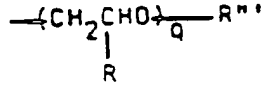
et pour laquelle chaque unité définie par a, b ou d est distribuée au hasard parmi le polymère.

4. Les polymères solubles dans l'eau selon la revendication 3, représentés par :



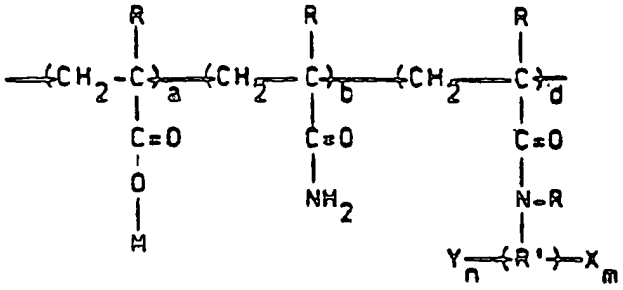
pour laquelle R' est un groupement de liaison hydrocarboné multivalent ayant de deux à 12 atomes de carbone, et lesquels sont choisis parmi les groupements alkyles linéaires ou ramifiés, aryles, alkaryles, cycliques et hétérocycliques et leurs mélanges ;

et où R" est un groupement alkyle linéaire ou ramifié, aryle, alkaryle, cyclique ou hétérocyclique hydrogénocarboné ayant de 1 à 20 atomes de carbone ou un groupement alkoxyle représenté par :

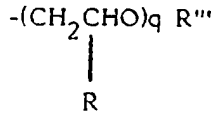


m = 0 à 10,
n = 1 à 10, prévoyant que la somme (m + n) = 1 à 2 ;
et ensuite pour laquelle (a + b + d), la somme, est suffisante pour obtenir un poid moléculaire de 1000 à 20.000.000, et M est H, un groupement alkyle inférieur (C_1-C_4), un métal alcalin, un ion ammonium ou leurs mélanges.

5. Les polymères solubles dans l'eau selon les revendications 3 ou 4 représentés par :



pour laquelle
R est un hydrogène ou un groupement alkyle inférieur (C_1-C_4) ;
R' est un groupement de liaison multivalent alkyle linéaire ou ramifié, aromatique, cyclique et ou hétérocyclique ayant de 1 à 8 atomes de carbone ; et
R" est un groupement substituant hydrocarboné ayant de 1 à 6 atomes de carbones ou un substituant alkoxylate représenté par

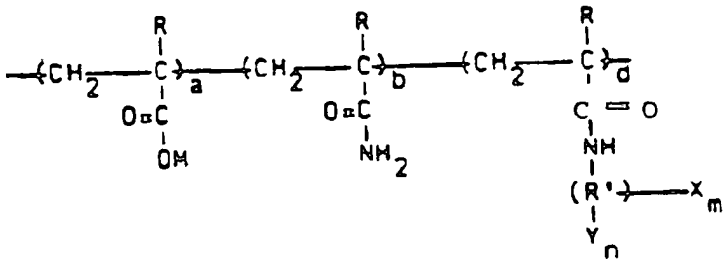


et leurs mélanges, et
M est H, Li, Na, K, NH_4 ou leurs mélanges, et
n = 1 à 8
m = 0 à 8, prévoyant que la somme, m + n = 1 – 10.

6. Les polymères solubles dans l'eau selon la revendication 5 pour lesquels :
R est un méthyle, R' est un groupement alkyle linéaire ou ramifié, aromatique et/ou cyclique et où p est 1, l'ion complémentaire est un chlorure, bromure, hydroxyle, et un méthylsulfate, et leurs mélanges ;

m	= 0 à 4
n	= 1 à 4, prévoyant m + n = 1 – 8 ;
(a + b)/d	= 0,01 – 50 et
q	= 1 à 25.

7. Les polymères solubles dans l'eau selon les revendications 1, 4 ou 5, représentés par :



pour laquelle

R est un hydrogène ou un méthyle ;

R' est un groupement alkyle linéaire ou ramifié ayant de 1 à 6 atomes de carbone ;

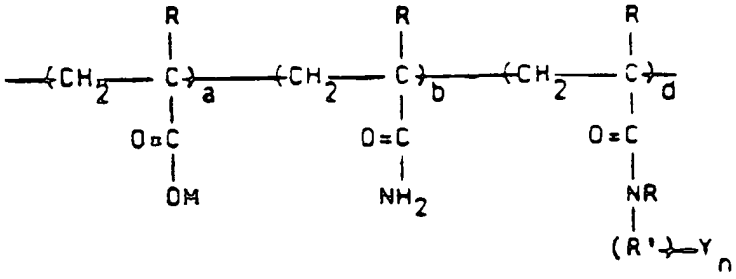
M est H, Li, Na, K, NH_4 et leurs mélanges ;

m = 1,

n = 1 – 6, et

q = 1 – 30.

8. Les polymères selon la revendication 3, représentés par :



pour laquelle

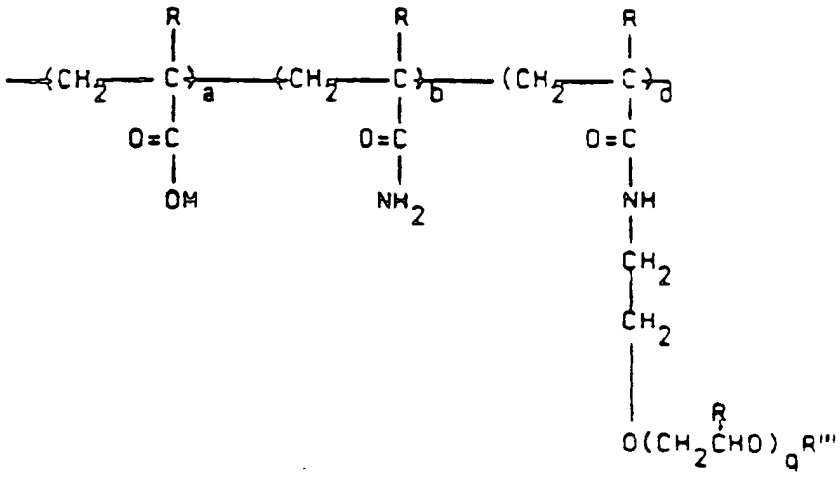
R est hydrogène ou un groupement alkyl inférieur (C_1-C_4) ;

R' est un groupement alkylène linéaire ou branché ayant de 1 à 6 atomes de carbone ;

M est H, Li, Na, K, NH_4, et leurs mélanges ;

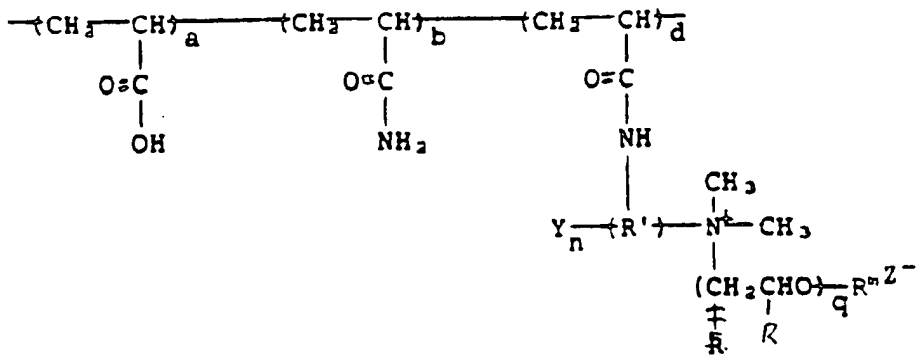
n = 1 – 6.

9. Les polymères selon la revendication 8, représentés par :



pour laquelle R est un hydrogène ou un groupement alkyle inférieur ayant de 1 à 4 atomes de carbone, et la somme, a + b + d, est suffisante pour obtenir un poids moléculaire de 1.000 à 20.000.0000.

10. Les polymères selon la revendication 7, représentés par :



pour laquelle

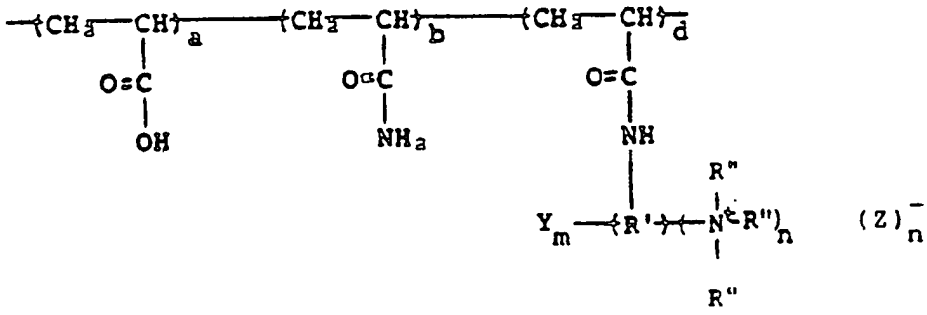
R' est un groupement hydrocarboné linéaire ou branché, contenant de 1 à 6 atomes de carbone ; Z^- et CL^-, Br^-, T^-, est leurs mélanges ;

R = H ou un groupement alkyl inférieur (C_1-C_4) ;

q = 0 – 30 ; et

n = 1 – 6.

11. Les polymères selon la revendication 7 ayant un poids moléculaire d'au moins 1.000, représenté par:



pour laquelle

R' est un groupement hydrocarboné linéaire ou ramifié contenant de 2 à 5 atomes de carbone ; Z^- est CL^-, Br^-, I^-, OH^-, méthylsulfate et leurs mélanges ;

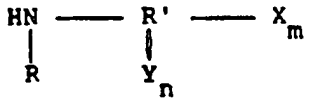
R" est un méthyle, éthyle, propyle, butyle et leurs isomères ;

R"' est un hydrogène et/ou un groupement alkyle inférieur (C_1-C_4) ;

m = 0 à 4 ; et

n = 1 à 4.

12. Procédé pour la production de polymères selon les revendications 1 à 11 par transamidation d'un polymère/copolymère contenant des groupements substituants amides fonctionnels avec un réactif chimique de formule :

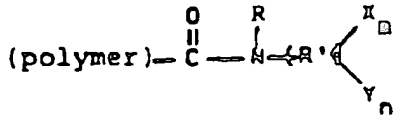


pour laquelle les substituants et indices ont les mêmes significations que dans les revendications 1 à 11.

13. L'utilisation des polymères selon les revendications 1 à 11 pour le traitement de l'eau comme dispersants, inhibiteurs de tartre, floculants, coagulants ou épaississants.

Revendications pour les Etats Contractants : AT, ES

1. Procédé pour la production de polymères solubles dans l'eau contenant des substituants amides, ayant un poids moléculaire d'au moins 500, lesquels ont au moins une mole pour cent de leurs groupements amides originaux convertis en une structure d'amides, substitués, représentés par :

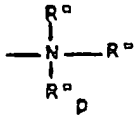


pour laquelle

R est choisi, pour chaque cas, parmi l'hydrogène ou un groupement alkyle inférieur (C_1-C_4)

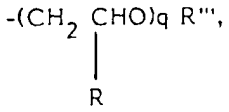
R' est un groupement de liaison hydrocarboné multtivalent ayant de 1 à 20 atomes de carbone et qui peut être un alkyle linéaire ou ramifié, un aryle, un alkaryle, un cycle ou un hétérocycle et leurs mélanges ;

X est représenté par la formule



pour laquelle

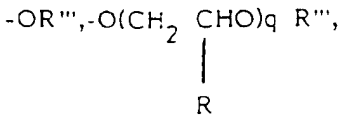
R" est un groupement hydrocarboné choisi pour chaque cas parmi les groupements alkyles linéaires ou ramifiés aryles, alkaryles, cycliques hétérocycliques, ou deux groupements R" pris ensemble pour former un cycle, les groupements alkoxyles représentés par



et leurs mélanges, et

R"' est individuellement choisi, pour chaque cas, parmi l'hydrogène, un groupement hydrocarboné ayant de 1 à 20 atomes de carbone et étant des groupements alkyles linéaires ou ramifiés, aryles et alkiaryles, des groupements cycliques et hétérocycliques et leurs mélanges ;

Y est choisi, pour chaque cas, parmi le groupe consistant en



et leurs mélanges, et

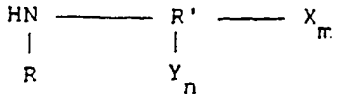
m = 0 – 20 et

n = 1 – 20,

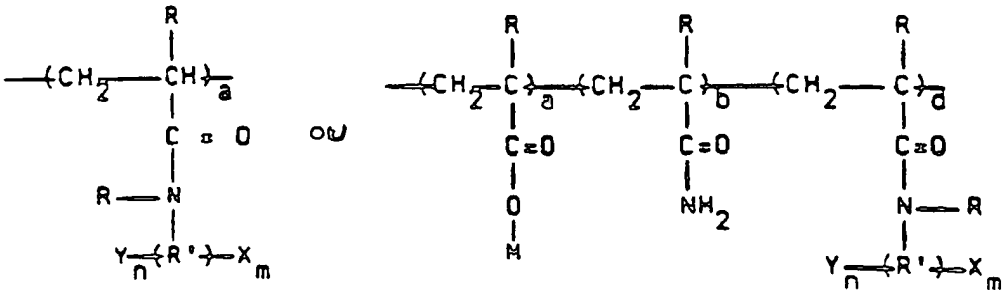
p est de 0 à 1, prévoyant que lorsque p est 1, un ion complémentaire électroneutralisant est présent en équivalence ;

q = 1 – 50.

par réaction de transamidation d'un polymère/copolymère contenant des groupements fonctionnels amides avec un réactif chimique de formule :



2. Procédé selon la revendication 1 pour la production de polymères dont au moins 1 mole pour cent de ces unités (métha) crylamides originales sont converties en unités de formule :



pour lesquelles les substituants et indices ont la même signification que dans la revendication 1, et M est H, un groupement alkyle en C_1 à C_4, un métal alcalin ou alcalino-terreux, un groupement ammonium ou ammonium-quatenaire, ou une amine primaire, secondaire ou tertiaire.

$a \geq 10$

$a + b + d$ est suffisant pour obtenir un poid moléculaire d'au moins 500 et

a/b	= jusqu'à 100 ;
a/d	= jusqu'à 100 ;
(a + b)/d	= 0,01 – 100 ; et
b/d	= 0,01 – 100

et pour lesquels les unités sont distribuées au hasard parmi le polymère.